Quantification and Analysis of Carbon Deposition on Catalytic Oxygen Carriers for the Oxidative Coupling of Methane

Undergraduate Research Thesis in Chemical Engineering

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Abstract

The current commercial method of obtaining ethylene, a highly valuable product, through steam cracking is highly process and energy intensive. An alternative way to obtain ethylene is through the direct conversion of natural gas to ethylene in a one step process through oxidative coupling of methane (OCM). A chemical looping scheme is an attractive mode of operation for OCM because of the enhanced selectivity towards ethylene made possible by a catalytic oxygen carrier (COC). However, a major concern for this process is carbon deposition, or "coking", which deactivates the COC by blocking active sites. Coking may be prominent in a OCM system, as the reactor is operated with limited supply of oxygen. Solid carbon compounds form and collect in the catalyst bed and are difficult to directly measure because they are not present in the reactor gas outlet. The goal of this project is to identify and quantify solid carbon formation using analytical techniques and to determine effects of carbon deposition on the performance of our COC for OCM. To quantify the solid carbon formation, COC samples were run for different time periods in the fixed bed reactor and analyzed using a carbon analyzer. After preliminary tests, carbon was detected on both fresh and used COC. Evaluating the amount of carbon deposition and the existence of other carbon compounds is the first step in learning how they form and a step toward reducing the amount of side reactions to increase the yield of ethylene in our system. This is also helpful in indicating the upper reaction time limit for our system before coking occurs.

Acknowledgements

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1. Introduction

1.1 Relevance/Motivation

The demand for ethylene, a valuable chemical commodity, has been increasing in recent years as seen in Figure 1 below[1]. To meet this demand, the chemical industry and researchers have investigated many ways to produce ethylene from low cost feedstocks.

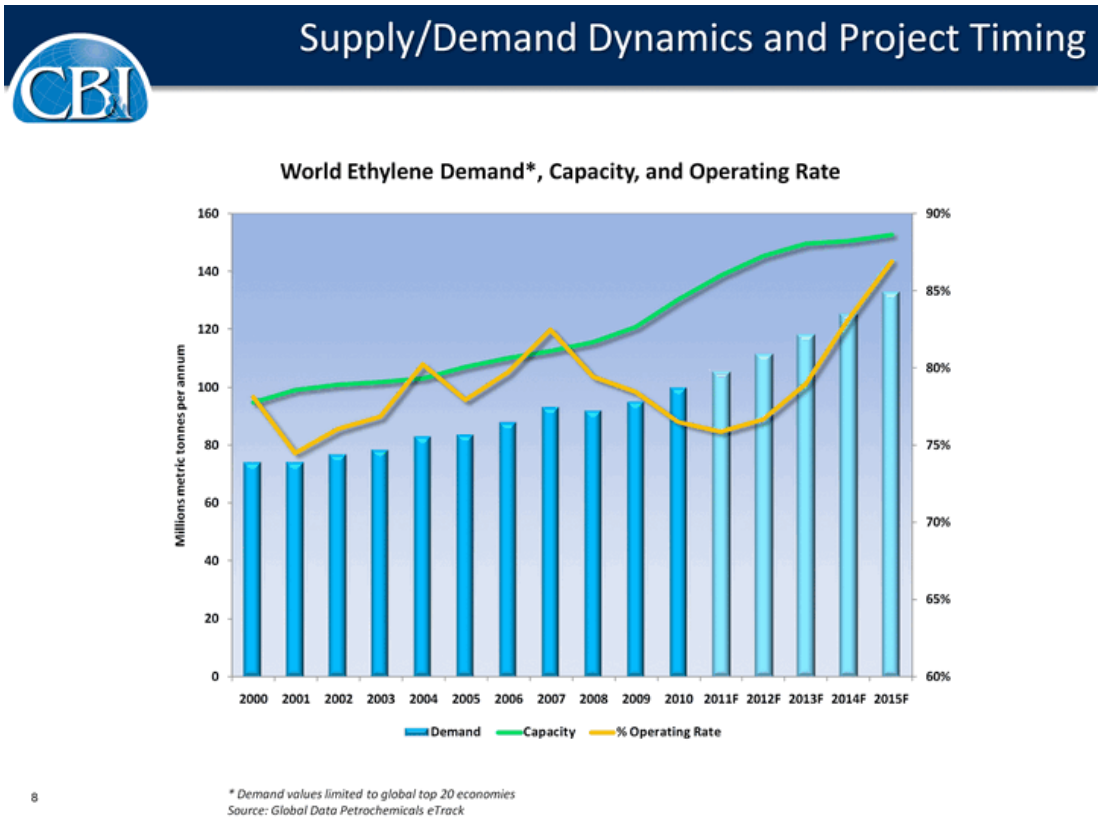

Figure 1: World Ethylene Demand by Year

Currently, the most common way to produce ethylene in the US is through the steam cracking of ethane and propane[2]. One major issue with steam cracking of ethane and

propane how energy and process intensive it is. The process of steam cracking is endothermic and therefore requires a large energy input to produce ethylene[3]. Currently, there are also no major advances seen in technology for steam cracking in the near term which creates value for alternative processes to produce ethylene[2].

There has been a large increase in the supply of natural gas in recent years due to hydraulic fracturing. Figure 2 shows the production of natural gas in the US is projected to increase to over 40 trillion cubic feet by 2040[4].

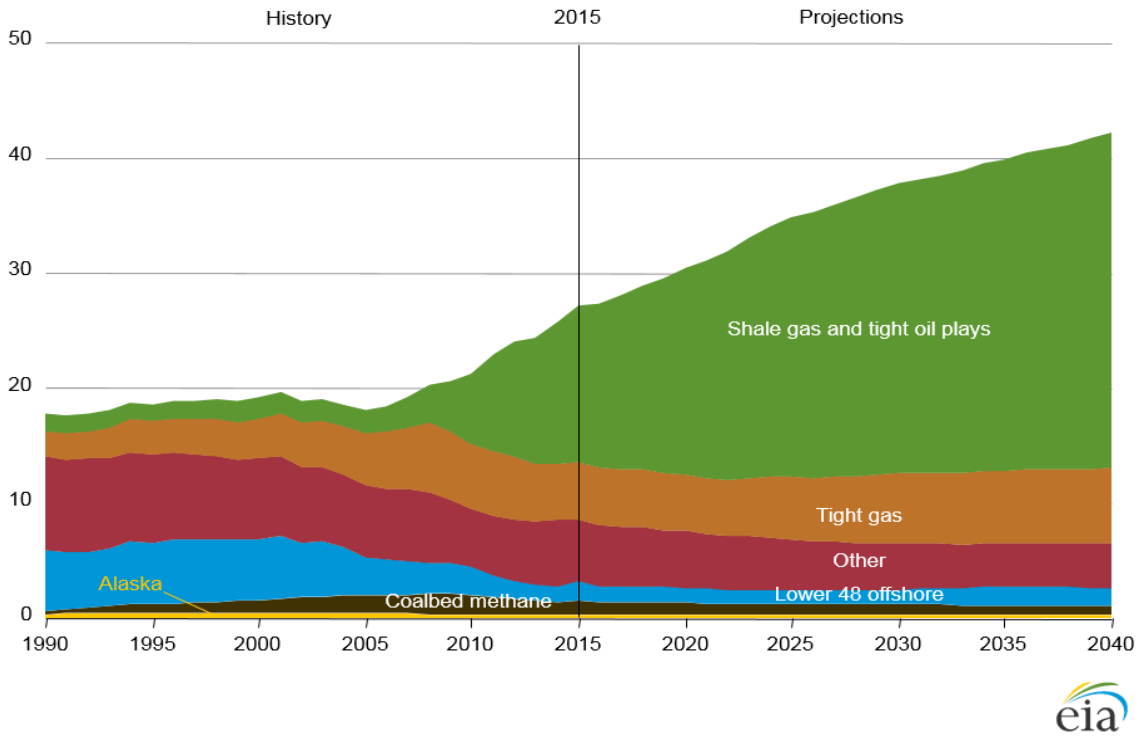

Figure 2: U.S. Dry Natural Gas Production by Source

With the supply of natural gas on the rise, the conversion of methane which usually comprises over 90 mole % of natural gas directly to ethylene is promising[5]. One way to directly convert methane to ethylene is through the Oxidative Coupling of Methane (OCM).

1.2 OCM Overview

Discovered by Keller and Bhasin, the Oxidative Coupling of Methane (OCM) is a series of reactions that directly converts methane into ethylene utilizing a catalyst or catalytic oxygen carrier (COC)[5]. OCM involves the selective oxidation of methane using either lattice oxygen on a metal oxide COC or molecular oxygen over a catalyst to produce a mixture of methane, carbon monoxide, carbon dioxide, and higher hydrocarbons. This process is most commonly carried out in one of two different conformations, "co-feed" or "redox"[6]. Co-feed involves a pure methane feed stream with an oxygen stream through a catalyst bed which oxidizes the methane with molecular oxygen and its mechanism is shown in Figure 3 below[6,7].

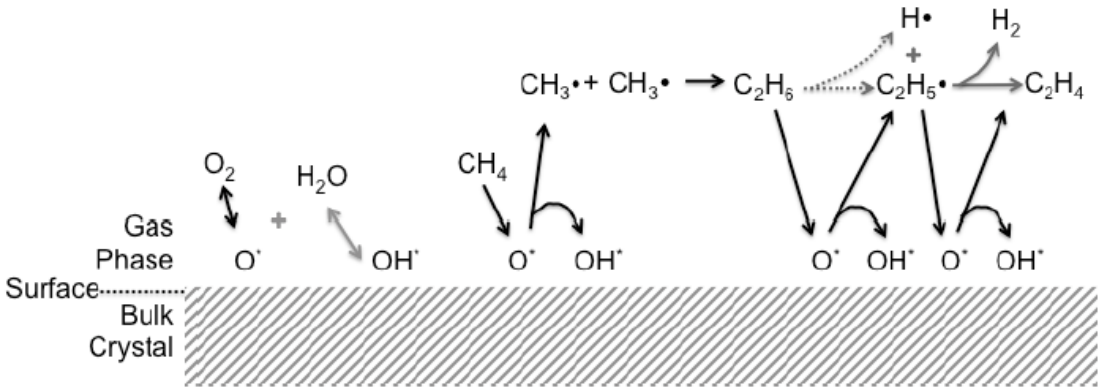

Figure 3: Co-Feed OCM Mechanism

Redox involves first sending a stream of air through the COC bed to oxidize the COC bed in an "oxidation step". After a nitrogen purge, a methane stream is sent through the COC bed and is oxidized by the lattice oxygen on the COC in the "reduction cycle". The method of which OCM was carried out in this study was in a redox conformation.

During the reduction phase in a redox conformation, methane reacts with the oxygen on the surface of the oxidized COC and reacts to form methyl radicals. These

methyl radicals combine to form ethane molecules which then also can react with the surface oxygen to form ethane radicals. These ethyl radicals can react with the surface oxygen or thermally react to form ethylene[6].

Overall, OCM is exothermic and gives off heat which is an advantage of this process over steam reformation. Carbon oxides form when hydrocarbons react with gaseous or lattice oxygen. Manganese oxide COC's have been known to give good OCM activity[8]. Doping COC's with lithium have also shown promise in the past[9]. This study is investigating the features of Mg_6MnO_8 (MMO) and a lithium doped version, $Li_{0.2}Mg_{5.8}MnO_8$ (LiMMO).

1.3 Coke Formation Background

The formation of solid carbon deposition or "coke" a common occurrence in hydrocarbon processes under low oxygen conditions. The carbon deposition forms on the surface of the catalyst similarly to how it would form on the surface of a COC and reduces its activity for OCM[10]. By deactivating the COC, the coke inhibits the selective oxidation reaction which leads to lower yields of higher hydrocarbons. In addition, since the carbon deposition is formed in the solid phase from the methane feed, there is less carbon in the gas phase which also lowers the yield of higher hydrocarbons by decreasing the selectivity of desired products. It has also been suggested that the formation of coke increases with an increase in surface area on the COC[8,11].

Thermodynamically, coke is the favored product in absence of oxygen as seen in Figure 4 on the following page. During the reduction step, Mg_6MnO_8 is reduced to Mg_6MnO_7. This results in the reduction of Mn(IV) in Mg_6MnO_8 to Mn(II) in Mg_6MnO_7.

Therefore, oxygen available for reduction in the COC accounts for only 4.9% of the mass of fully oxidized MMO. This limited amount of oxygen is important for OCM due to the issue of over oxidation of products if there is too much oxygen in the system. Because of the limited oxygen in the system, MMO is quickly reduced under methane. This allows for the possibility of an oxygen deficient system which would allow the formation for coke within a short duration of reduction.

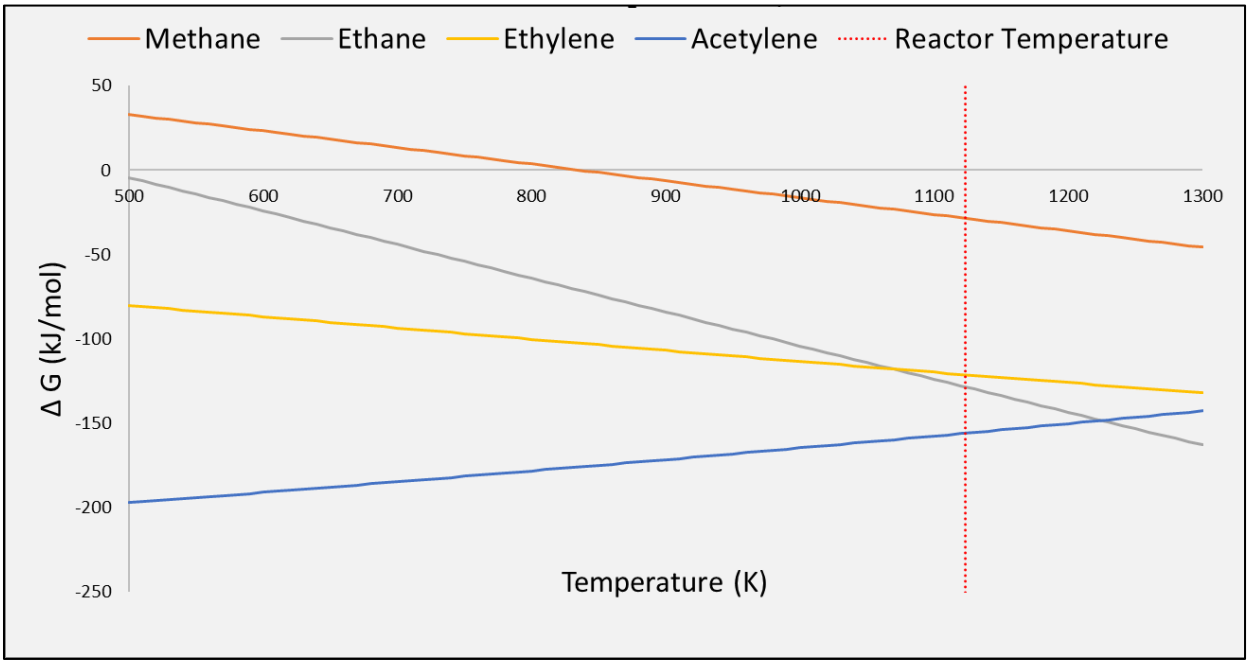

Figure 4: Coke Formation Thermodynamics

1.4 CM5015 Coulometer Theory

The CM5015 Coulometer determines carbon content of samples utilizing an electrochemical cell and a photodetector. The photodetector is used to determine the percent transmittance of light through the cathode solution which is proportional to the amount of CO_2 formed from combusting carbon in the sample. The samples are combusted in a furnace at 900 °C under oxygen which converts all carbon compounds into CO_2. The

CO_2 is then sent to the cathode of the electrochemical cell shown below on the left in Figure 5[12].

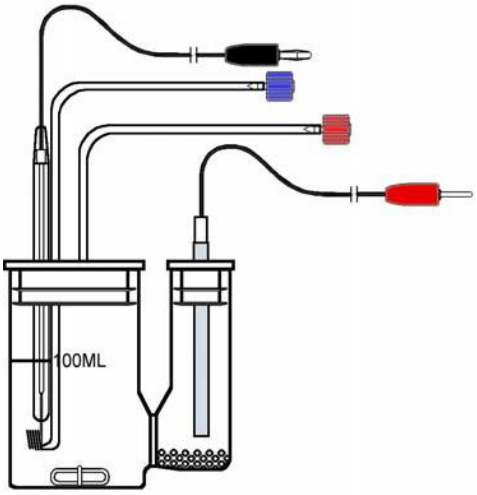

Figure 5: CM5015 Coulometer Electrochemical Cell

The overall reaction in the electrochemical cell is a redox reaction described below[12].

Cathode Reactions

1. Absorption of CO_2 by cathode solution

$$CO_2 + HOCH_2CH_2NH_2 \rightarrow HOCH_2CH_2NHCOOH$$

2. Electrochemical Generation of OH^- (cathode reaction)

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$$

3. Neutralization of absorbed CO_2 reaction product by electrochemically generated OH^-

$$HOCH_2CH_2NHCOOH + OH^- \rightarrow HOCH_2CH_2NHCOO^- + H_2O$$

Anode Reaction

$$Ag^\circ \rightarrow Ag^+ + e^-$$

2. Experimental Methodology

2.1 COC Synthesis

The MMO COC was synthesized from MgO and MnO_2 in stoichiometric amounts. The Lithium doped MMO was synthesized in the same way but with the addition of LiOH in a stoichiometric quantity to produce $Li_{0.2}Mg_{5.8}MnO_8$. Powders of MgO, MnO_2, and LiOH were mixed in water and dried. The mixtures were calcined under air at 950 °C for 10 hours.

2.2 Fixed Bed Setup

This study utilized a fixed bed with 100% methane as the reduction gas and air as the oxidizing gas with nitrogen gas purges in between. The reactor setup for the fixed bed experiments is shown in Figure 6 on the next page. Initially, the COC's were loaded into the fixed bed and heated to 850 ºC in air. Nitrogen was then sent into the reactor to purge gas phase oxygen for 10 minutes.

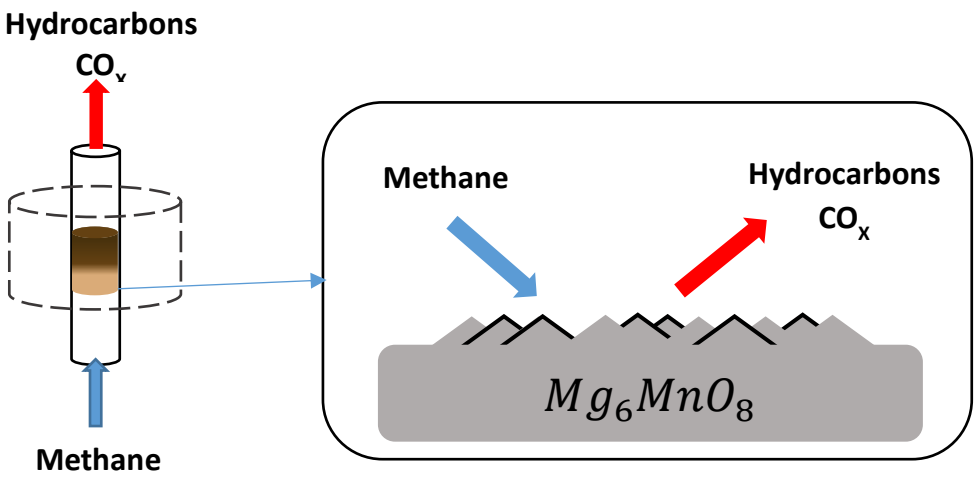

Figure 6: Reactor Setup

The samples were run for 5 cycles before being taken out during the reduction step on the 6th cycle. The steps for the initial 5 cycles are shown in Table 1 below. Two reduction times were tested for the 6th cycle, 15 and 30 seconds. The fixed bed reactor conditions are summarized in Table 2 on the next page.

Table 1: Fixed Bed Cycle Steps

Fixed Bed Cycle Steps		
Step	Gas	Time
Step 1	Methane	15 seconds
Step 2	Nitrogen	10 minutes
Step 3	Air	30 minutes
Step 4	Nitrogen	10 minutes
Return to step 1		

Table 2: Fixed Bed Reactor Conditions

Fixed Bed Reactor Conditions	
Pressure	1 atm
Temperature	850 °C
GHSV	2400 hr^{-1}
COC Particle Size	300-850 µm

After reaction, the samples were cooled to room temperature under nitrogen. The samples were split into an upper and lower half after they were removed. These samples were then tested for carbon content using the CM5015 Coulometer.

2.3 Coulometer Setup

The CM5015 Coulometer, show on the next page in Figure 7, was used to measure the amount of carbon in each sample[12]. The furnace connected to the CM5015 Coulometer was heated to 900 °C under pure oxygen at a flow rate of 125 ml/min. The oxygen was sent through a 40% KOH scrubber solution to remove any CO_2 from the oxygen carrier gas. The samples were then placed into the furnace, after running a blank test for calibration, and to fully combust any carbon present in the sample. The gas from the sample then flowed through a barium chromate catalyst/scrubber which ensures the complete oxidation of carbon to CO_2. The gas then was sent through a magnesium perchlorate post-scrubber which acts as a desiccant to remove moisture. The gas was then finally sent through a NO_x scrubber consisting of acid dichromate and MnO_2 to remove any NO_x products before being

sent to the coulometer[13]. The sample was analyzed for 45 minutes to ensure all carbon was combusted.

Figure 7: CM5015 Coulometer

2.4 Thermogravimetric Analyzer Setup

For the thermogravimetric analyzer (TGA) studies, the SETSYS Evolution TGA, shown on the next page in Figure 8, was utilized[14]. The samples were loaded into the TGA and heated under air to a reaction temperature of 850 °C. In the experiment, both fresh and activated MMO and LiMMO were tested. The COC's were activated through redox cycles in the TGA for 15 cycles described on the next page on Table 3.

Figure 8: SETSYS Evolution TGA

Table 3: TGA Cycle Steps

TGA Cycle Steps		
Step	Gas	Time
Step 1	Air	30 minutes
Step 2	Nitrogen	5 minutes
Step 3	10% Methane	5 minutes
Step 4	Nitrogen	5 minutes
Go back to step 1		

3. Results and Discussion

3.1 TGA Results

The TGA experiments show a detailed profile of the COC weights under different conditions vs time. The time was scaled so that all graphs started approximately 2 minutes before the switch to the nitrogen stream. The percent weight over time graph was the percent weight of the COC compared to the weight of the COC at time zero.

Figure 9 on the following page shows the results from the TGA test for the fresh COC's. Even after over 30 minutes of methane reduction, there was no indication of coke formation for either COC. Each section shown below correlates to which gas stream was fed into the TGA in the cycle during that time. As seen in both Figure 9 and Figure 10 on the following pages, the COC weight was stable under air. The weight started to decrease under nitrogen due to oxygen uncoupling because Mn(IV) is a Chemical Looping Oxygen Uncoupling (CLOU) material[15].

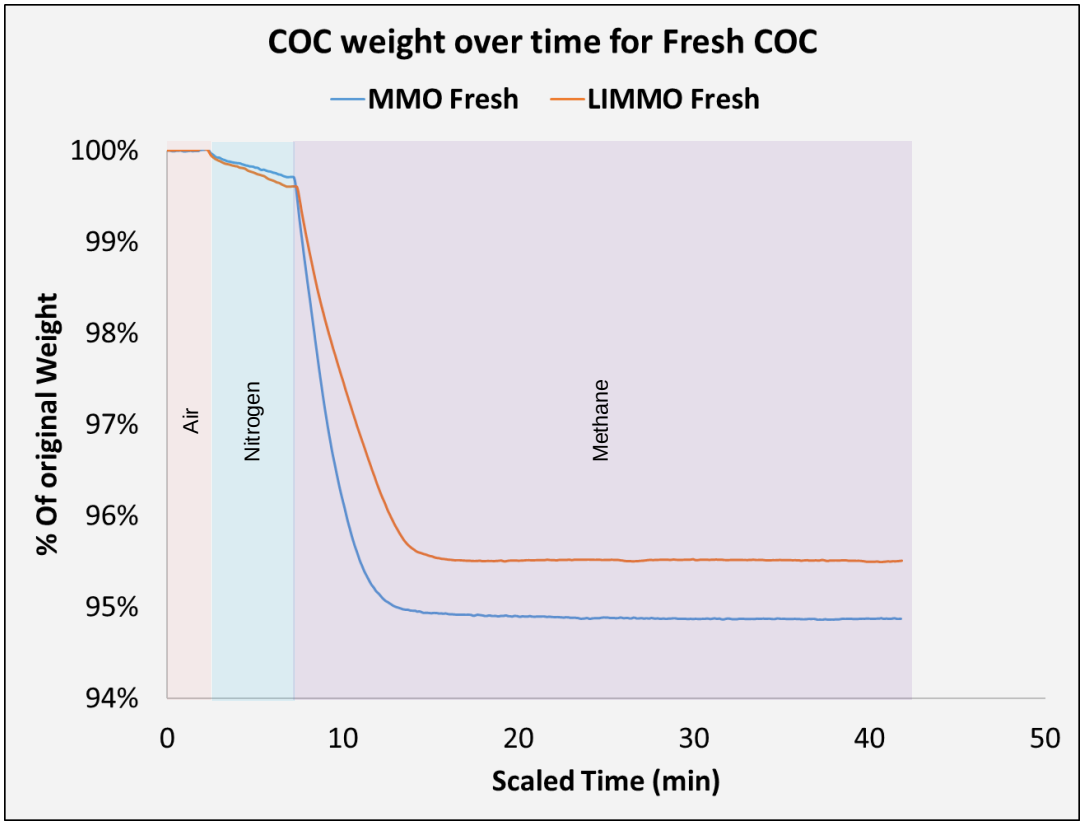

Figure 9: TGA Data for Fresh COC's

The TGA results for the activated COC's are shown on the next page on Figure 10. Both activated COC's show coke formation after around 10 minutes of methane reduction. According to the results, activated LiMMO is more prone to coking than MMO by a factor of approximately 15 indicated by Table 4 on the next page.

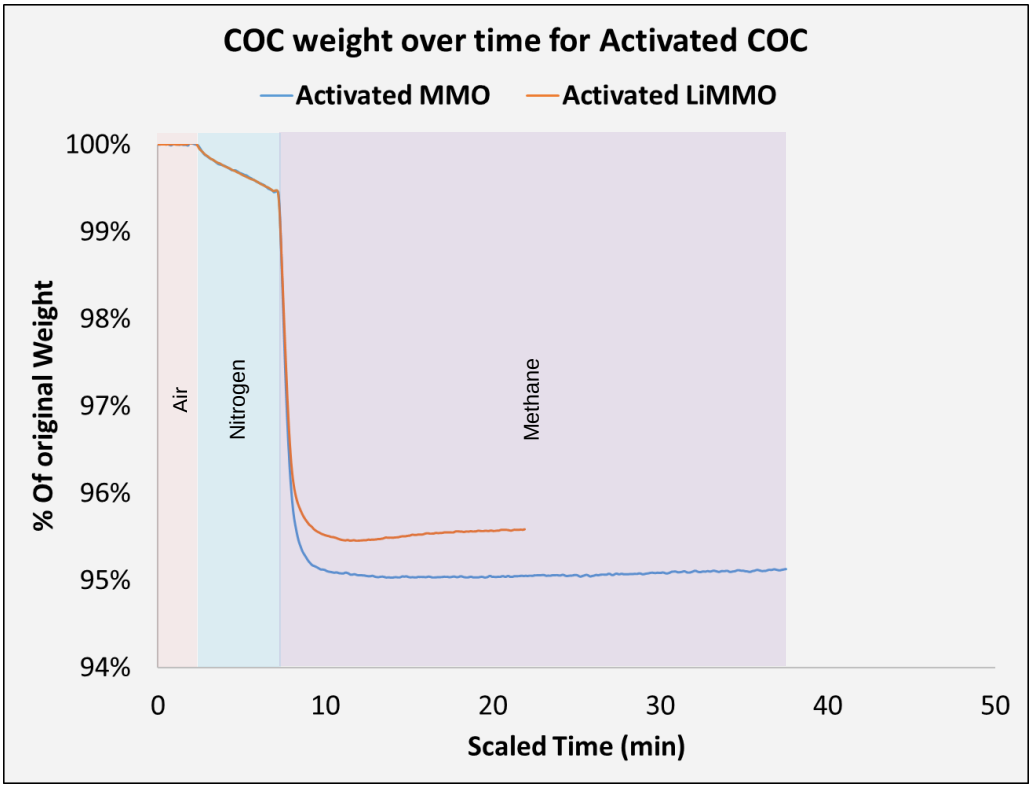

Figure 10: TGA Data for COC Activated after 15 Cycles

Table 4: Carbon Deposition in the TGA

Carbon Deposition in the TGA	
COC Type	Carbon Deposition at 20 Minutes
Fresh MMO	0.000%
Fresh LiMMO	0.000%
Activated MMO	0.009%
Activated LiMMO	0.132%

3.2 Carbon Analyzer Results

Based on the TGA studies, it is expected that LiMMO would show a higher amount of coke formation in the fixed bed compared to MMO. As seen in Figure 11 below, MMO is shown to be more prone to coking than LiMMO after both being reduced for 15 and 30 seconds in contrast to the TGA study. For 15 second reduction, MMO shows 107% more carbon formation compared to LiMMO. For 30 second reduction, there a lower difference in carbon formation with MMO showing 11% more coke formation than LiMMO. This difference in results between the two instruments is elaborated upon in the next section.

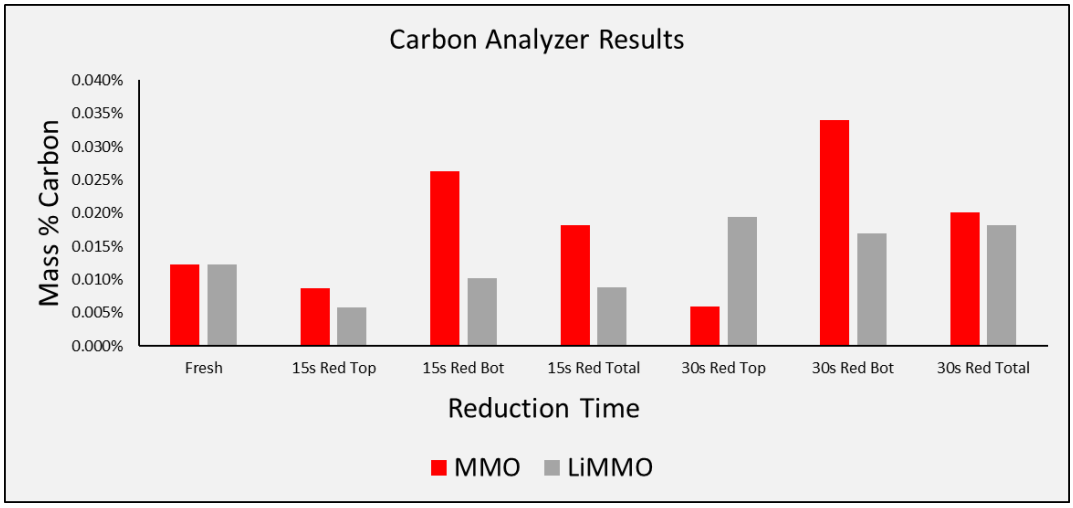

Figure 11: Carbon Analyzer Results

It was also hypothesized that the top and bottom section of the fixed bed would have different amounts of coke formation. It is expected that the bottom half of the fixed bed would have more carbon content than the top due to the orientation of the reactor. This can be explained by the fact that in the fixed bed system, the methane flows from the bottom of the reactor which reduces it much more quickly due being exposed to a pure methane stream. This indicates that coking is more likely to form on the bottom half of the bed

compared to the top. It is seen that the bottom portion of each sample contains more carbon deposition than the top portion for all reacted samples.

Based on the results, the fixed bed reactor system does not have a significant amount of coke formation at 15 seconds. Therefore, a 15 second reduction step is a reasonable limit for the system with LiMMO and MMO before the formation of coke becomes significant.

3.3 Comparison of TGA and Carbon Analyzer results

Although the direct carbon content from the TGA and fixed bed studies cannot be directly compared due to the differences in the systems, the trends between the different COC's can be compared in each system. The TGA studies indicated that LiMMO is more prone to carbon deposition while the fixed bed study indicated the opposite, that MMO is more prone to coke formation.

One explanation is due to the inconsistencies in activation of the COC's between the two studies. Over multiple cycles, the COC's become "activated" possibly through a change in their morphology. ActivatioNon of the COC's change their reactivity towards OCM[8]. Although both the TGA and fixed bed studies tested COC's after multiple prior redox cycles, it is not clear whether the COC's were activated after this time, particularly in the fixed bed due to different layers of the COC's reacting at different rates. In the TGA, it is assumed that the COC's react uniformly. It can be hypothesized that MMO and LiMMO require different amounts of cycles to activate. There is a possibility that LiMMO was not activated in the fixed bed after 5 cycles and was activated in the TGA study. This

may explain why MMO was less prone to coke formation than LiMMO was in the fixed bed system but not the TGA.

4. Conclusion and Future Work

Two COC's for OCM were synthesized and tested under various conditions for the presence of carbon deposition. The COC's were tested for carbon deposition in both a fixed bed system and a TGA system for OCM.

In the TGA system, neither of the fresh COC's showed indication of coke formation after over 25 minutes of methane reduction. However, both activated COC's showed the presence of coke after 10 minutes of methane reduction. LiMMO showed significantly more coke formation compared to MMO.

For the fixed bed experiments at a reduction time of 15 seconds on the 6^{th} cycle, LiMMO did not show evidence of increased carbon content when compared to the fresh sample. MMO, however, showed an increase in carbon content compared to fresh MMO. At a 30 second reduction time on the 6^{th} cycle, both samples showed an increase in carbon content. LiMMO and MMO had a similar carbon content at 30 seconds of methane reduction with MMO having slightly more carbon deposition. These results indicate that MMO is more prone to coke formation with the current reactor system. It should be noted that these results indicate a very small amount of coke formation in the at 15 seconds of reduction. Therefore 15 seconds of reduction is a reasonable limit for the system before coke formation becomes significant.

However, it is hypothesized that there may be an increase in coke formation with an increase in activation and cycles. To test this hypothesis, further studies to test the effect

of additional cycles will be conducted. To determine other possible carbon formation on the COC's, energy-dispersive X-ray spectroscopy will be utilized. In addition, multiple dopants that show reactivity towards OCM will be tested for coke formation in future work. Although the current system has minimal coke formation, with longer reduction times coke formation may become an issue. For future work with longer reduction times, studies will be conducted on the effect of the addition steam and CO_2 to the reduction phase cofed with methane to reduce the amount of coke formation.

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